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### **Process for Production of Powder Grains**

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The invention concerns the production of explosive fuels, in particular that of rocket powder grains.

Very large propellant grains for application as rocket powder for military purposes or for application in take-off rockets supported by jet propulsion in airplanes usually possess grain diameters of 2.5 cm or several times this amount and on occasion lengths greater than 30 cm. Hitherto, such large grains were produced through extrusion of the explosive mass,

after which the latter was transformed into the form of gelatinized sheets. For the production of these sheets a number of rolling processes were required, wherein the removal of volatile material took place during the final rolling processes or through subsequent drying. The gelatinization was effected through rolling out, which frequently was supported by intermediate kneading processes, the rollers usually being heated. The explosive material sheet or carpet so obtained was then rolled together into a bundle and put into the extrusion form.

This process suffers from the disadvantage that it requires very large extruders, rollers, etc. for the equipment that serves the processing of the explosive material, which equipment can produce extremely high pressures, and that the operation goes forth in the best case only very slowly and under dangerous conditions, so that many precautions must be taken in order to avoid an explosion during the extruding. If the mass contains nitroglycerin, then during the lengthy rolling process a considerable amount of nitroglycerin can be lost through evaporation, which leads to fluctuations in the composition of the grains finally obtained. Such large grain fuels have also already been produced through casting methods; these casting methods, previously known, likewise have disadvantages. Thus, for example, a casting process is known, in which powder grains on a two-component basis, whose surfaces have been made sticky by aid of a softening agent, are pressed to a homogeneous powder grain and heated. Such a process is indeed well suited for certain types of large grains, but is not suitable for the production of grains on a one-component basis; further, it requires the application of pressure with the associated dangers and is not suitable for the production of grains of an irregular form, such as are required for adaptation to certain types of rocket motors for attainment of the desired type of ballistic operation.

One purpose of the invention is the creation of a simplified and improved process for producing rocket powder grains, which process avoids the disadvantages of the known processes. A further object of the invention is the creation of a process for producing rocket powder grains on a one- or two-component basis without use of a rolling process or another type of application of pressure and without the devices required for this. Further, the invention aims to create an improved casting process for producing rocket powder grains of any form or type whatever.

The process according to the invention for producing powder grains through the generation of a pourable paste is characterized by the fact that one first of all mixes gelatinized nitrocellulose fuel particles with at least 25 volume percent of a liquid or liquefied softening

agent for the nitrocellulose at temperature at which practically no dissolving of the nitrocellulose particles into the softening agent takes place, and that one heats the mixture to a temperature sufficient for the dissolving of the nitrocellulose into the softening agent, in particular in the region of 50 to 90°C, long enough for the particles to have completely gone into solution and for a homogeneous mass to have formed, upon which one shapes this mass into a powder grain.

The shaping process can take place through a pouring of the paste into a mold or through another type of shaping, whereupon the mixture is held in the desired form long until the paste has hardened or has become firm and the desired powder grain has been formed. The hardening process is preferably carried out at a higher temperature, in order to accelerate it. Otherwise, the shaping can also occur through a heating of the paste to a higher temperature, at which the softening agent dissolves the fuel, the extruding of the heated mass through a form into a continuous strand, and the dividing of the so-formed pressed piece or rod into the lengths required for the powder grains. The higher temperature speeds up the dissolving of the fuel and facilitates the extrusion of the mixture. Under "liquid softening agent" is understood here a relatively non-volatile fluid that represents a slow-acting solvent at low temperatures or usual room temperature for the ball-shaped particles of the fuel or one that exerts no or only a minimal dissolving capability on these, but which at higher temperatures acts quickly and possesses a relatively strong dissolving capability for the tiny fuel balls.

It has been found that the fuel grains can be advantageously produced through the stirring of nitrocellulose and a solvent for the latter, such as ethyl acetate, with an excess of non-solvent, such as water, in the presence of a protective colloid, the removal of the solvent, and subsequent drying of the ball-shaped nitrocellulose particles so obtained. Ball-shaped particles of greater density are, according to the invention, especially advantageous, since even in the dried state they flow relatively freely and possess a "case hardened" surface that withstands the initial attack by the solvent. This surface quality is no doubt the result of a "skin effect" that is caused by the surface tension and the removal of the solvent upon the formation of the balls. Together with the nitrocellulose, in the formation of the ball-shaped particles still other components, such as dioctylphthalate, lead stearate, minium, centralite, soot, dinitrotoluene, and the like, can be added, in order to lend the powder the desired ballistic characteristics. By using such ball-shaped particles, one obtains a relatively freely flowing paste when the balls are mixed in the correct mass proportion with the plastisol solvent, whereas one does not attain this freely flowing condition of the paste when

irregularly shaped particles are used, such as are obtained, for example, by simple milling of gun powder or the like. Although the fuel balls can have any desired size, for balls of large diameter a relatively long period of time is required in order to achieve their dissolving and hardening of the grains conditioned thereupon, while with smaller balls the times are correspondingly shorter. Preferably, then, one works with balls of a diameter of no greater than approximately 0.127 mm and in particular of a much smaller diameter, e.g. 0.0254 mm or less.

The usual liquid modification means are solvents for nitrocellulose and are outstandingly suitable as liquid softening agents in the process according to the invention, the only necessity being that the modification means have a relatively weak solvent power for the fuel at the usual room temperature or at lower temperatures. In other words, the solvent power of the fluid softening agent should not be so great that during the time required for the uniform mixing of the solvent and the fuel and for the forming of the mixture so obtained an appreciable dissolving of the fuel takes place at normal temperatures. If one wishes to produce rocket powder grains on a two-component basis, then one can mix energy-delivering modification means, such as nitroglycerin, butantrioltrinitrate, diglycoldinitrate, ethyleneglycoldinitrate, and the like, with one or more stabilizing means that are mixable therewith, such as dibutylphthalate, dimethylsebacate, dibutylsuccinate, dibutyladipate, triacetin, ethyldiphenylphosphate, tributylphosphate, and the like, whereby one obtains a fluid softening agent that is outstandingly suitable for the purpose according to the invention. If one wishes to produce rocket powder grains on a one-component basis, then one can leave energy-delivering modification means out of the mass, and in this case the liquid softening agent consists merely of the liquid stabilizing means, which can consist of one of the above mentioned materials or a mixture of these. Other stabilizing means suitable to the same purpose at temperatures above their melting points are dimethylphthalate, dioctylsebacate, o-nitrobiphenyl, butylbenzylphthalate, octyldiphenylphosphate, triethyleneglycoldi-2-ethylbutyrate (i.e. triglycoldihexoate) and the like.

The mass of the liquid softening agent should amount to at least approximately 25 volume percent of the mixture of solvent and fuel. The use of substantially smaller amounts of liquid softening agent leads to the formation of hollow spaces and air pockets in the rocket grains, and mixtures with such lower amounts of softening agent are generally not fluid enough for the present purpose. Larger amounts of liquid softening agent can be used to advantage in order to increase the fluidity of the mixture, to change the ballistic characteristics of the

rocket grains, and to ensure the absence of hollow spaces and air pockets in the grains; however, the amount used should preferably not be so large that the fuel precipitates or settles during the time required for hardening.

In operation, the liquid softening agent is preferably dried or otherwise treated, in order to bring any possible traces of moisture to a minimal level, and both the fuel and the liquid softening agent are preferably evacuated for several hours before the mixing to an absolute pressure of 10 mm Hg or less, and then homogeneously mixed together in a suitable mixer, e.g. a mixer with sigma-shaped agitators, in which process the pressure is likewise held at 10 mm Hg or less, whereupon one pours the mixture into a mold or otherwise shapes it in such a manner that air inclusions are avoided and rocket powder grains of the desired shape are obtained. The precautions of drying and evacuating are preferably taken, in order to attain, to the extent possible, rocket powder grains that are free of hollow spaces. In the pouring process for shaping the grains, after the mixture has been transformed into the desired shape, heat is introduced in order to increase the temperature of the mixture preferably to a region between about 50 to 90° C, and this temperature is maintained until the fuel is dissolved and the mixture has hardened, whereupon the temperature is lowered. In the extrusion process for producing the grains, the mixture is preferably heated to a temperature in the range of 50 to 90° C, until the fuel is dissolved, whereupon the heated mass is squeezed out through a die. In general, the rule holds good that one requires a shorter time in the pouring process to achieve a satisfactory hardening of the grain, or in the extrusion process to bring about the dissolving of the fuel, and requires a lower pressure to subsequently push the mixture through the extrusion die, the higher the temperature is; however, great care must be taken that the combustion or explosion temperature of the mixture is not exceeded. If in the extrusion method the fuel is dissolved into the liquid softening agent, the hot mass is squeezed out through an extrusion die, so that a continuous strand of explosive exits from the extrusion die. The heating of the mixture can take place through the use of a heated worm or screw feed that propels the mixture through the extrusion die, the dwell time in the feed device being long enough for the mixture to be heated and the dissolving of the fuel to be brought about. The extruded strand is then cut up in suitable lengths into powder grains that possess a uniform composition throughout.

The following example serves to illustrate a typical implementation form of the invention. 250 parts nitrocellulose with a nitrogen content of approximately 12.6% are mixed with 4100 parts water of approximately 50° C to a watery slurry. Separately from this, a slurry of soot in ethylacetate is produced, in which at first 0.705 parts soot are thoroughly mixed

with 100 parts ethylacetate. The mixture of soot and ethylacetate is then added to a further 1250 parts ethylacetate and the diluted mixture of soot and ethylacetate is stirred, in order to ensure the uniform distribution of the suspended soot particles. Thereupon, one combines the mixture of soot and ethylacetate with 31.4 parts dinitrotoluene and 2.8 parts ethylcentralite. As soon as the dinitrotoluene and ethylcentralite have dissolved, the mixture is stirred into the nitrocellulose slurry. Then the temperature is raised to 68° C and the entire batch is vigorously stirred for one hour, by which time the nitrocellulose will have gone into solution. Then 25 parts of a protective colloid (derived from an animal protein) are added, dispersed in 150 parts water, whereupon one further stirs the mixture until the nitrocellulose solution has been shaped into small balls of the desired small particle size. For the formation of much smaller particles, intense stirring is required. The addition of a emulsifying agent, e.g. the water-soluble salts of fatty acids, sulfonated oils, the so-called water-soluble oils, and the like, makes the formation of small particles from the nitrocellulose solution considerably easier, and for this reason one adds to the bath 24 parts of a 40% aqueous solution of the sodium sulfate derivative of 2-ethylhexanol. Next, one adds in the course of an hour a solution of 125 parts sodium sulfate in 300 parts water and stirs an additional 3 hours. The small balls are then hardened into powder grains through the removal of the ethylacetate by continuous stirring and heating up to approximately 99° C. The ball-shaped fuel grains so obtained are then dried in the air at 50° C and consist of approximately 87.7% nitrocellulose, 11.0% dinitrotoluene, 0.3% soot and 1.0% ethylcentralite, and possess an average grain diameter of approximately 0.0254 mm, which depends more or less on the intensity of the stirring during the formation of the grains.

Approximately 56.18 parts by weight of the ball-shaped fuel grains are then introduced into a mixer with sigma-shaped agitators, and the system is evacuated to an absolute pressure of approximately 10 mm Hg and kept at this pressure for 16 hours. In the meantime, one puts 37 parts by weight of a practically water-free liquid softening agent, consisting of 74 weight percent nitroglycerin, 25 weight percent dimethylphthalate, and 1 weight percent ethylcentralite, into a vessel, evacuates this vessel to an absolute pressure of approximately 10 mm Hg and holds it under this vacuum for approximately 16 hrs. Then the liquid softening agent is added to the fuel in the mixer and the mixer activated, so that the liquid softening agent and the fuel are thoroughly mixed; the vacuum is maintained here in order to prevent the formation of air pockets.

### First Shaping Stage: Casting

As soon as the liquid softening agent and the fuel are uniformly mixed together, the mixture is shaped by being carefully poured into a mold, pockets of air being avoided; the mold consists of a synthetic material that is resistant to nitroglycerin, such as cellulose acetate, methylmethacrylate, or ethylcellulose. Since the liquid softening agent has a specific gravity of approximately 1.5, the volume share of the liquid softening agent in the mixture amounts to approximately 41.3%.

The mold with the mixture of liquid softening agent and fuel is then placed into an oven at 75° C and kept at this temperature until the fuel has been more or less dissolved by the liquid softening agent and the grain has hardened. This dissolving and hardening of the grain can easily be managed in a relatively short time, but can also take place overnight. The precise time of this heat treatment naturally depends on the degree of effectiveness of the liquid softening agent, the grain size of the fuel, and the effective power of resistance of the surface of the fuel grains, which was designated above as "case hardening". By using the above described fuel and liquid softening agent, the mixture becomes hardened, when one leaves it at the relatively low temperature of about 22° C for example, typically in approximately 21 hours. When the grain has become hard, one lets it cool off at room temperature and removes it from the mold.

### Second Shaping Stage: Extrusion

Since the liquid softening agent has a specific gravity of about 1.5, the volume share of the liquid softening agent in the mixture amounts to approximately 41.3%. After liquid softening agent has been uniformly mixed with the fuel, the mixture is carefully poured or otherwise brought into a heated worm or screw feed device, e.g. a "moyno" pump, which presses the mixture through an extrusion die. The length of the screw feed device and the speed at which the mixture exits the extrusion die are preferably controlled in such a manner that the mixture, on its way from one end of the screw to the other, towards the extrusion opening, is heated sufficiently to achieve a virtually complete dissolving of the fuel. In this way, one can carry out the operation on a continuous basis. In order to achieve this, the screw feed mechanism is kept at a temperature of approximately 75 to 85° C and the feed velocity of the supply as well as the exit velocity from the extrusion opening are appropriately controlled so that the fuel goes into solution. The precise length of time of the heat



treatment required for this can vary from a few minutes up to several hours and depends on the degree of effectiveness of the liquid softening agent, the temperature of the mixture, the grain size of the fuel, and the effective resistance of the surface of the fuel grains, which was designated above as "case hardness"; in any case, however, the mixture is held at a higher temperature until the fuel has gone into solution and the mass has sufficiently hardened that the desired powder grains can be formed. As the gelatinized mass is pressed out of the extrusion die, it is cut up into powder grains of the desired length.

Rocket powder grains produced according to the above example are practically free of undesired hollow spaces, practically uniform in their composition throughout the entire grain, and possess the solidity and the other physical characteristics that are required for rocket powder grains. It is evident that the process is relatively simple, is suitable for mass production, and requires no costly equipment such as is necessary to develop high pressures. It is further evident that the fuel and the plastisol solvent can vary considerably in their composition, and that according to the invention one can produce rocket powder grains of practically any desired ballistic quality.

## PATENT CLAIMS

1. Process for producing powder grains by making a pourable paste, **characterized by the fact that first of all gelatinized nitrocellulose fuel particles are mixed together with at least 25 volume percent of a liquid or liquefied softening agent for the nitrocellulose at a temperature at which practically no dissolving of the nitrocellulose particles into the softening agent takes place, and by the fact that the mixture is heated at a temperature sufficient for the dissolving of the nitrocellulose in the softening agent, specifically from 50 to 90° C, until the particles have gone completely into solution and a homogeneous mass has formed, whereupon the mass is shaped into a powder grain.**
2. Process according to Claim 1, **characterized by the fact that ball-shaped nitrocellulose particles of an average diameter of less than approximately 0.127 mm are used.**
3. Process according to Claim 1 or 2, **characterized by the fact that the liquid softening agent contains an energy-delivering modification means for the fuel grains.**
4. Process according to Claims 1 through 3, **characterized by the fact that the mixture is poured into a mold and held at a temperature at which the nitrocellulose goes into solution, until the nitrocellulose has completely gone into solution and the homogeneous mass thus obtained has hardened into a powder grain.**
5. Process according to Claim 4, **characterized by the fact that the mass is held in the mold at atmospheric pressure.**
6. Process according to Claims 1 through 3, **characterized by the fact that the practically homogeneous mass that is obtained after the heating of the mixture for the complete dissolving of the nitrocellulose is pressed out in a heated state through an extruder and the strand is cut up into powder grains.**

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Documents taken into consideration:

German Patent Specifications 337 461, 337 495

British Patent Specifications 639 204, 756 771, 757 129